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(21) International Application Number: PCT/AU89/00105 (22) International Filing Date: 17 March 1989 (17.03.89) (31) Priority Application Number: PI 7361 (32) Priority Date: 17 March 1988 (17.03.88) (33) Priority Country: AU (71) Applicant (for all designated States except US): COM-ALCO ALUMINIUM LIMITED [AU/AU]; 55 Collins Street, Melbourne, VIC 3000 (AU). (72) Inventor; and (75) Inventor/Applicant (for US only) : MAY, Robin, Frank [AU/AU]; 2 Kiandra Close, Greensborough, VIC 3088 (AU). (74) Agent: SMITH SHELSTON BEADLE; 207 Riversdale Road, Hawthorn, VIC 3122 (AU).		(81) Designated States: AT (European patent), AU, BE (European patent), BR, CH (European patent), DE (European patent), FI, FR (European patent), GB (European patent), IT (European patent), JP, LU (European patent), NL (European patent), NO, SE (European patent), US. Published <i>With international search report.</i>
(54) Title: METALLIC SURFACE PROTECTION (57) Abstract A process of treating corrosive liquids to protect metallic surfaces exposed to such liquids, comprising the step of increasing the redox potential of the corrosive liquid, for example, by means of hydrogen peroxyde, before it contacts the metallic surface to be protected, whereby the process liquid causes the formation of a protected oxide layer on said metallic surface.		

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METALLIC SURFACE PROTECTION**FIELD OF THE INVENTION:**

This invention relates to the treatment of chemical process liquids which cause corrosion, and ultimately, stress corrosion cracking, of metallic surfaces exposed to such liquids.

BACKGROUND OF THE INVENTION:

Ferrous materials, including both plain and alloyed carbon steels, are susceptible to a corrosion phenomena known as stress corrosion cracking (SCC) or caustic embrittlement when exposed to hot caustic liquors. This can cause significant problems in industrial plants utilizing hot caustic liquors for processing. For example, alumina refineries (e.g. Bayer plants) which digest bauxite ores in sodium hydroxide at temperatures up to 300°C use plain carbon pressure vessel steels for pipework and vessels in the liquor stream. Similarly, pulp digesters in the paper industry are exposed to the same type of environment.

Plain carbon and alloy steels remain relatively inert under these conditions due to the formation of protective oxides and scales. They are, however, sensitive to stress corrosion cracking, a process involving selective intergranular or transgranular attack which penetrates deep into the metal structure. SCC occurs under a range of specific conditions in the process stream and has been loosely allied to liquor temperature, caustic strength and stress level in the metal. The incidence and intensity of attack increases with increasing levels of the three factors.

As the name SCC implies, the stress factor is an important factor in the mechanism of attack. Stresses can arise during fabrication (e.g. along weldments, bends, etc.) or can be introduced due to temperature and/or pressure fluctuations in the process stream.

Measures taken to avoid or reduce the risk of SCC include:

- i) post weld stress relief
- ii) temperature limits

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iii) caustic strength limits

iv) anodic protection (paper industry)

The specification of temperature and caustic limits reduces the range of operating conditions which can in turn limit plant productivity. Post weld stress relief is regarded as one of the most effective mitigation measures but cannot be controlled sufficiently to ensure full protection against SCC failures.

Considerable effort has also been directed towards developing cost-effective SCC resistant alloys but further work is required before this can be achieved.

BRIEF DESCRIPTION OF THE INVENTION AND OBJECTS:

It is an object of the present invention to provide a process of treating corrosive liquids to protect metallic surfaces exposed to such corrosive liquids against corrosion to thereby materially reduce the incidence of stress corrosion cracking.

The invention provides a process of treating corrosive liquids to protect metallic surfaces, and particularly ferrous metallic surfaces, exposed to such corrosive liquids, comprising the step of increasing the redox potential of the corrosive liquid before it contacts the metallic surface to be protected whereby the process liquid causes the formation of a protective oxide layer on the metallic surface.

The invention may be applied to any corrosive liquid and is particularly applicable to hot caustic liquids. The process of the invention results in the metallic surfaces contacted by the treated caustic liquid being passivated by the formation of the protective oxide layer, which in turn substantially alleviates the problem of stress corrosion cracking.

The invention is specifically applicable to the treatment of Bayer process liquors to reduce the incidence of stress corrosion cracking of plant materials contacted by the process liquors. However, the invention is equally applicable to other corrosive liquors in other industries, such as the paper industry.

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The step of increasing the redox potential of the corrosive liquid may be achieved by the addition of any suitable oxidizing agent to the corrosive liquid. Suitable oxidizing agents include H_2O_2 , $NaHO_2$, O_2 , O_3 , $NaNO_2$ and $KMnO_4$. Such oxidizing agents increase the redox potential of the liquid which in turn promotes passivity of the metallic surface.

Brief Description of the Drawings:

A preferred embodiment of the invention will now be described with reference to the accompanying drawings in which:

Figure 1 is a graph showing the effect of caustic concentration and temperature on SCC plain carbon steel in Bayer liquor, and

Figure 2 is a graph shown the effect of H_2O_2 addition SCC sensitivity.

Description of Preferred Embodiment:

In the Bayer process sodium hydroxide is used to dissolve alumina from the bauxite ore at temperatures up to $300^\circ C$. The so-called pregnant liquor is subsequently cooled to $100^\circ C$ through a series of flash tanks and settled and filtered to remove the insoluble residue. Alumina is then precipitated from the caustic liquor which is reheated in a series of heaters and returned to the digester. Following the precipitation the recycled liquor is referred to as spent-liquor and it is this liquor which contributes predominantly to stress corrosion damage.

The components in the spent liquor circuit susceptible to SCC include the heater tubes and tube sheets and the interconnecting pipework between each heater. The latter are particularly sensitive to SCC along weldments. In general welds are stress relieved to reduce the risk of SCC.

The incidence and intensity of SCC in this part of the circuit has been found to increase along the heater chain as the temperature of the liquor increases.

Treatment of the process liquor is preferably performed at the low temperature side of the spent liquor circuit, but it may also be undertaken to advantage at the high

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temperature and if organic impurity (e.g. humates) control is required in the process stream. Where the oxidizing agent is H_2O_2 , an effective concentration range in quiescent spent liquor required for protection against SCC at $160^\circ C$ is 0.05 - 1.5% (V/V), or 50 - 3,000 mg per litre of spent liquor and preferably in the range 200 - 1,000 mg per litre of spent liquor. At lower temperatures the amount of H_2O_2 required will be considerably less. Conversely, the level will increase with increased caustic concentration and temperatures. Similarly, any increase or decrease in the organic impurity level in the process stream will require a corresponding adjustment in the level of H_2O_2 required for protection.

Modifications in the chemistry of the peroxide solutions may also be made to increase the stability of the peroxide and thereby reduce the level required for SCC mitigation. Alternatively, other more potent oxidants may be used to produce the same result.

TESTING:

The effectiveness of oxidant dosing to reduce SCC was assessed using a slow strain technique, known as slow strain rate testing (SSRT) which is an accelerated test for SCC sensitivity. This technique is accepted as a useful test for identifying the stress corrosion resistance of metals but cannot be used to determine time to failure. Tensile specimens are strained to failure at a constant rate (10^{-6} sec^{-1}) in a known tensile testing machine.

The reduction in cross sectional area measured at the time of failure gives a direct indication of the ductility of the metal. For example, if the reduction in area of a medium carbon steel exceeds 50%, the failure can be considered ductile and the stress corrosion component can be assumed to have had a minimal effect on failure. Conversely, when the reduction in cross sectional area is less than 50%, the stress corrosion component can be considered a primary contributory factor in the failure mechanism.

In the following examples, the threshold level for SCC of a typical pressure vessel steel in Bayer liquors is

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established for a range of liquor temperatures and caustic concentrations together with the effect of hydrogen peroxide dosing on material exposed to caustic liquors above the threshold level.

EXAMPLE 1:

Using the SSRT technique, the effect of liquor concentration and temperature on the stress corrosion sensitivity of a typical pressure vessel steel (Table 1) was established.

Table 1 - Composition of Pressure Vessel Quality Steel

Composition wt %					
C	Mn	P	S	Si	Fe
0.31	0.85	0.035	0.04	0.05	Rem.
to					
1.25					

The spent liquor used for the tests was taken from the spent liquor circuit of an alumina refinery (Table 2).

Table 2 - Analysis of Spent Liquor

		<u>Caustic</u>	
		<u>g/l</u>	<u>Ratio</u>
1.	Alumina	84.8	0.378
2.	Caustic Soda (as Na ₂ CO ₃)	224.4	-
3.	Total Soda	262.9	-
4.	Total Sodium	326.8	-
5.	P ₂ O ₅	0.11	0.0005
6.	P ₂ O ₅ as Soda	0.25	-
7.	SiO ₂	0.47	0.0021
8.	SiO ₂ as Soda	0.83	-
9.	V ₂ O ₅	0.80	0.0036
10.	V ₂ O ₅ as Soda	1.40	-
11.	NaCl	14.32	0.0638
12.	NaCl as Soda	12.99	-
13.	Na ₂ SO ₄	0.32	0.0014
14.	Na ₂ SO ₄ as Soda	0.24	-
15.	Non Caustic Soda	102.4	0.456
16.	Carbonate Soda	38.5	0.172
17.	Non Alkaline Soda	63.9	0.285
18.	Sodium Oxalate	3.19	0.014

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19. Oxalate as Soda	2.52	-
20. Total Inorganic Non Alkaline Soda	15.71	0.070
21. Total Organic Soda	45.67	0.204
22. TOOC as Soda	226.0	1.007
23. Fe ₂ O ₃	0.004	-
24. C/3	0.854	-
25. S/Total Sodium	0.804	-
26. Kelly Soda	311.0	-

The results shown in the graph of Figure 1 clearly identify the temperature and caustic concentration above which SCC can be expected. At normal caustic concentrations (225 g/l expressed as caustic soda) the threshold temperature for SCC is 150°C. At 160°C, SCC can be expected to occur in ferrous components stressed close to or beyond the yield point of the material.

Micrographic analysis shows that for SCC non-sensitive regions the fractures under testing are ductile, while SCC sensitive regions the fractures under testing are brittle. The extent of SCC propagation penetrating into the samples from the outer surface was noted to be unacceptable above the threshold temperature. The micrographs also show the marked difference in the reduction of cross-sectional area under the two conditions.

EXAMPLE 2:

Taking 160°C as a representative temperature at which SCC will dominate the failure mechanism, tensile samples were exposed to liquors containing increasing levels of hydrogen peroxide. The effect of these additions on the reduction in cross-sectional area at the time of failure and, therefore, the mode of failure is shown in the graph of Fig. 2.

These results demonstrate the increasing benefit of peroxide additions at 160°C and also show that stress corrosion can be mitigated even at higher caustic concentrations. In the latter case the potency of the peroxide must be increased to reduce the dosing level. This may be improved by adding stabilizers to the peroxide to reduce the rate of decomposition to O₂ and H₂O.

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CLAIMS:

1. A process of treating corrosive liquids to protect metallic surfaces, and particularly ferrous metallic surfaces, exposed to such corrosive liquids, comprising the step of increasing the redox potential of the corrosive liquid before it contacts the metallic surface to be protected whereby the process liquid causes the formation of a protective oxide layer on the metallic surface.

2. The process of claim 1, wherein the step of increasing the redox potential of the corrosive liquid is achieved by the addition of an oxidizing agent to the liquid.

3. The process of claim 2, wherein the oxidizing agent is selected from H_2O_2 , $NaHO_2$, O_2 , O_3 , $NaNO_2$ and $KMnO_4$.

4. A process of treating corrosive liquids used in the Bayer process, comprising the step of adding to the liquor used in the process a material which increases the redox potential of the liquor to such an extent that a protective oxide layer is formed on metallic surfaces contacted by said liquor.

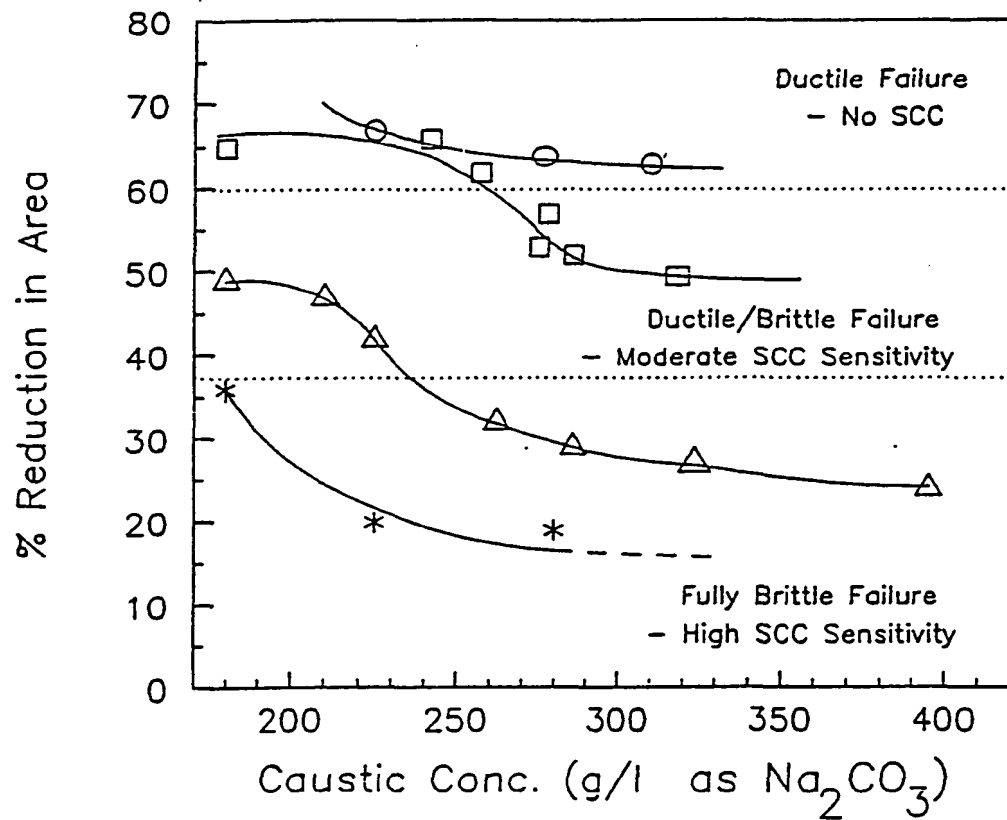
5. The process of claim 4 wherein said material is selected from H_2O_2 , $NaHO_2$, O_2 , O_3 , $NaNO_2$ and $KMnO_4$.

6. The process of claim 4, wherein said material is H_2O_2 and is added to the spent liquor circuit of the process therefore temperature of the spent liquor exceeds about $160^\circ C$ at a concentration of approximately 0.05 to 1.5% v/v (50 to 3000 mg/l of spent liquor).

7. The process of claim 6 wherein said concentration is 200 to 1000 mg/l of spent liquor.

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○ 140°C

□ 150°C

△ 160°C

* 180°C

Fig. 1

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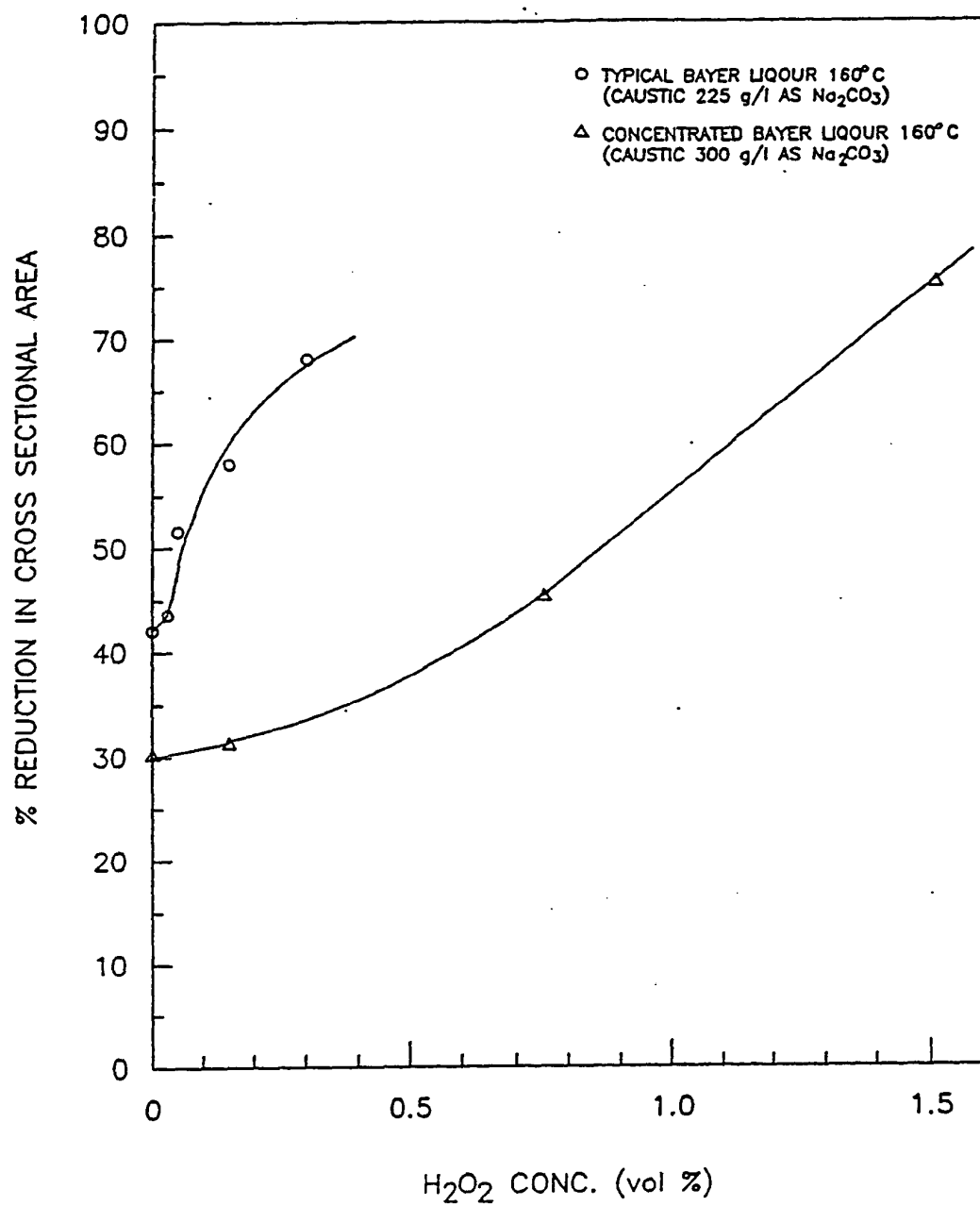


Fig. 2

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INTERNATIONAL SEARCH REPORT

International Application No. PCT/AU 89/00105

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) * According to International Patent Classification (IPC) or to both National Classification and IPC <div style="text-align: center; font-size: 1.2em;">Int. Cl.⁴ C23F 11/06, 11/18</div>						
II. FIELDS SEARCHED <div style="text-align: center; font-size: 0.8em;">Minimum Documentation Searched *</div> <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 25%; padding: 5px;">Classification System</td> <td style="padding: 5px;">Classification Symbols</td> </tr> <tr> <td style="padding: 5px;">IPC US CL</td> <td style="padding: 5px;">C23F 11/06, 11/18 422/12, 422/13</td> </tr> </table> <div style="text-align: center; font-size: 0.8em;">Documentation Searched other than Minimum Documentation * to the Extent that such Documents are Included in the Fields Searched *</div>			Classification System	Classification Symbols	IPC US CL	C23F 11/06, 11/18 422/12, 422/13
Classification System	Classification Symbols					
IPC US CL	C23F 11/06, 11/18 422/12, 422/13					
AU: IPC as above						
III. DOCUMENTS CONSIDERED TO BE RELEVANT *						
Category *	Citation of Document, ** with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³				
X	US,A, 1765344 (PIETZSCH et al) 17 June 1930 (17.06.30)	(1-3)				
X	GB,A, 1142317 (EICKMEYER) 5 February 1969 (05.02.69)	(1-3)				
X	US,A, 3721526 (FOROULTS et al) 20 March 1973 (20.03.73)	(1-3)				
X	GB,A, 1433298 (THE BENFIELD CORPORATION) 22 April 1976 (22.04.76)	(1-3)				
X	AU,B, 68346/74 (479763) (IMPERIAL CHEMICAL INDUSTRIES LTD) 30 October 1975 (30.10.75)	(1-2)				
X	AU,B, 29749/77 (514258) (DOW CHEMICAL CO.) 26 April 1979 (26.04.79)	(1-3)				
X	GB,A, 1579307 (W R GRACE & CO.) 19 November 1980 (19.11.80)	(1-3)				
X	Patents Abstracts of Japan, C-83, page 159, JP,A, 56-119783 (SUMITOMO KINZOKU KOGYO KK) 19 September 1981 (19.09.81)	(1-2)				
X	Patents Abstracts of Japan, C-347, page 19, JP,A, 60-258484 (MITSUBISHI JUKOGYO KK) 20 December 1985 (20.12.85)	(1-3)				
(continued)						
<table style="width: 100%; font-size: 0.8em;"> <tr> <td style="width: 50%; vertical-align: top;"> * Special categories of cited documents: ¹⁰ "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed </td> <td style="width: 50%; vertical-align: top;"> "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "G" document member of the same patent family </td> </tr> </table>			* Special categories of cited documents: ¹⁰ "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "G" document member of the same patent family		
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IV. CERTIFICATION						
Date of the Actual Completion of the International Search <div style="text-align: center; font-size: 1.1em;">30 May 1989 (30.05.89)</div>		Date of Mailing of this International Search Report <div style="text-align: center; font-size: 1.1em;">15 June 1989 (15.06.89)</div>				
International Searching Authority <div style="text-align: center; font-size: 1.1em;">Australian Patent Office</div>		Signature of Authorized Officer <div style="text-align: center;"> <div style="display: flex; justify-content: space-between; align-items: center;"> <div style="font-size: 0.8em;">A.W. WINCH</div> </div> </div>				

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

X	US,A, 4443340 (MAY et al) 17 April 1984 (17.04.84)	(1-2)
X	EP,A, 96151 (MONTEDISON SPA) 21 December 1983 (21.12.83) (& US,A, 4758311)	(1-3)
X	Derwent Abstract Accession No 87-261507/37, Class Q51, JP,A, 61-24872 (HITACH KK) 6 February 1986. (06.02.86)	(1-3)

V. ☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE :

This International search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. ☐ Claim numbers because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claim numbers because they relate to parts of the International application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claim numbers because they are dependent claims and are not drafted in accordance with the second and third sentences of PCT Rule 6.4(a).

VI. ☐ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING :

This International Searching Authority found multiple inventions in this International application as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International search report covers all searchable claims of the International application.
2. ☐ As only some of the required additional search fees were timely paid by the applicant, this International search report covers only those claims of the International application for which fees were paid, specifically claims:
3. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:
4. ☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

- ☐ The additional search fees were accompanied by applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

